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Session on Zinc-Air Batteries

ADVANCED PRIMARY ZINC-AIR BATTERIES

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The zinc-air battery system was selected to be a new member of the standard family of military batteries because of its many advantages as a power source. Among these advantages over other types of batteries are:

1. High energy density (over 100 watt hours/lb).
2. Good power density.
3. Elimination of electrical recharging.
4. Long unactivated shelf life.
5. Full environmental capability.
6. Reasonable cost.

The conceptual design for the standard family of mechanically rechargeable zinc-air batteries was first presented to this conference in 1967.[1] This design provided for a 20 cell unit using the 12.2″ × 4″ cross section of the standard battery box and the standard connector for the 6-12 volt or 12-24 volt output. Sufficient space was allowed at one end of the battery box for the connector and an assembly clamping mechanism. Air flow was achieved by natural convection. Battery BA-525 ( )/U, the 20 Ah size is illustrated in Fig. 1. Each cell, having a nominal load voltage of 1.2 volts consists of two air

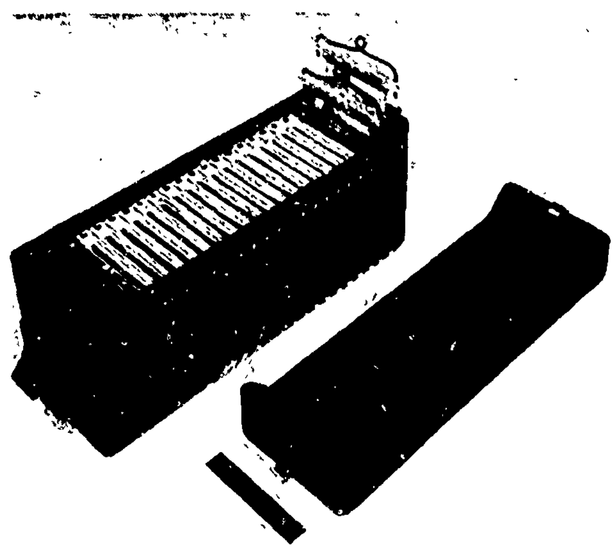

Figure 1. Zinc-Air Battery BA-525 ( )/U.

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cathodes connected in parallel and supported by a plastic frame. The resulting unit cell provides an air breathing but water tight box as the cell structure. A porous zinc anode enclosed in absorbent separator material is positioned between the cathodes. The KOH electrolyte is absorbed mainly in the porous anode and separator material. The battery is activated by addition of water to each of the cells and insertion of the anode-electrolyte composite which contains the potassium hydroxide in a solid form.

During the past two years, batteries and components have been fabricated and tested and the capability of the zinc-air battery to meet the design objectives, both electrical and environmental, has been demonstrated. The studies have resulted in the design of five (5) standard line mechanically rechargeable zinc-air batteries ranging in capacity from 20 Ah to 150 Ah. This range should adequately cover the power and energy levels required for the military application of these batteries. The design details of these five batteries are given in Table I.

Standard Battery Design Considerations

In the design of these batteries a number of features were considered, to attain optimum performance over the wide military operational range and achieve maximum interchangeability of parts. The performance of the mechanically rechargeable battery is known to be influenced by the amount of zinc present, the availability of water, the proper air flow and the surface area of the electrodes. Proper balance of these factors was necessary to obtain optimum performance and high energy output from —40°F to 130°F over a wide power range, on continuous or intermittent discharges, for required activated stand time.

The new designs cover a wide variety of improvements and component modifications. The main features are discussed below:

1. Water reservoirs. In many of the applications of the zinc-air battery, particularly at heavy loads, high operating temperatures and discharges over extended periods, it was found that performance of the battery was not limited by the capacity of the zinc anode, but by the lack of water in the cells. Moisture loss occurs through water vapor pick-up by the drier air flowing between cells. Battery discharge conditions, which cause excessive heat, increase water vapor pressure and air flow both of which result in increased water loss. In order to provide sufficient water for cell discharge under strenuous conditions the cell cavity was increased in volume and a water reservoir located at each side of the cell. Figure 2 shows the new cell with the water reservoir compared to the original cell design on the left. A water reservoir of this type is incorporated in each of the standard line cells. Suitable screens, intercell separators and other devices are added to the cathode design to minimize water evaporation and loss.

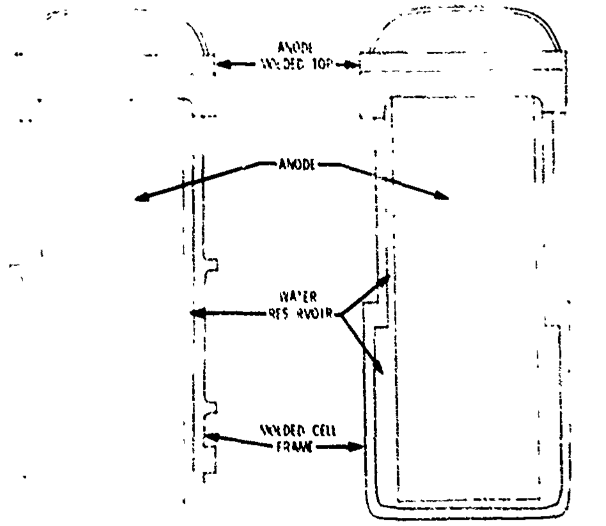


Figure 2. Cell Outline Showing Reservoir Compartments for Extra Water or Electrolyte.

2. Cathode/Anode seal and anode top design. A positive seal at the anode/cathode interface is essential for a leakproof design. This closure too must be designed to permit easy insertion and withdrawal of the anode from the cathode unit cell. To achieve this capability an horizontal I.D.-O.D. seal was designed and the cathode frame strengthened. An O-ring located in a retaining groove is used to complete the seal. In addition, the battery cover closes tightly on the anode top to

TABLE I

CHARACTERISTICS OF STANDARD FAMILY MECHANICALLY RECHARGEABLE ZINC-AIR BATTERIES BATTERIES

NOMENCLATURE	BA-525 ( )/U	BA-526 ( )/U	BA-527 ( )/U	BA-530 ( )/U	BA-528 ( )/U
VOLTAGE	12/24	12/24	12/24	12/24	12/24
DIMENSIONS (Inches)					
Length	12.2	12.2	12.2	12.2	12.2
Width	4.0	4.0	4.0	6.7	6.7
Height	4.8	7.0	9.0	7.3	10.0
WEIGHT (lbs) (Without Cover)	7.0	10.0	15.0	21.0	35.0
RATED CAPACITY (Watt-hours)	480.0	768.0	1152.0	1800.0	3000.0
ENERGY DENSITY (Wh/lb)	69.0	77.0	77.0	86.0	86.0

prevent any upward movement of the anode. Designs are currently under consideration for an anode having a molded handle integral with the top rather than attached separately.

3. Zinc-anode electrolyte composite. The anode thickness was increased to 0.230 inches. This allows sufficient zinc for the required capacity and also provides high porosity and adequate room for water.

4. Standard connector. The use of the standard six (6) pin 6/12 or 12/24 volt connector is employed on each of the standard line batteries. Using this connector either of two voltages can be obtained. The connector system also protects equipment from overvoltage. For example, six volt equipment will meet open circuit voltage conditions if plugged into a 12/24 volt battery if both are equipped with the standard line connector system.

5. Clamping mechanism. The batteries currently employ a screw device to apply sufficient lateral pressure to the cells after activation and insertion of the zinc anodes. The pressure on the cells is actually brought about through the flexibility of cell components and their compression to a fixed spacing or volume. New cathode and anode designs will permit the use of a simple two position open-closed knob to loosen the cells for activation and for removal of anodes and to tighten them to the necessary pressure for proper battery operation.

6. Type I, Type II Standard Line. At the 21st Annual Power Sources Conference, it was mentioned that two size batteries, the 20 and the 48 Ah would probably handle most of the military requirements. It since has been found necessary to expand the line of batteries to five (5) and, in order to provide efficient configurations and volume utilization, two standard line types were established. The Type I is most familiar being the manpack configuration which has the 12.2" × 4" cross-section. The Type II configuration is the portable configuration and has a cross section of 12.2" × 6.75". In each case, anode capacity and required electrode surface area govern the battery height. Limiting the batteries to these two designs enhances the interchangeability of component parts. For example, the anodes for all Type I batteries are identical, except for the height of the anode active material. Similarly, the cathode unit cells differ only in their height. Again, the designs of the Type I and Type II are similiar in configuration, but do differ in width as well as height. Anode and cell thickness and other related dimensions as well as battery hardware are identical for all batteries simplifying manufacture of the batteries and components and minimizing inventory of parts.

7. Environmental requirements. The zinc-air batteries must be capable of meeting stringent environmental conditions expected to be encountered in typical military operations. The battery case is thus fabricated from reinforced resin impregnated fibreglass and the cell assembly sufficiently supported to successfully resist damage from vibration, bounce and drop requirements specified for military use. Environmental tests conducted on these batteries confirm the adequacy of the mechanical design. The details of the new designs and requirements are specified in Electronics Command Development Description EL-CP2000-0038A.

Battery Electrical Test Data

Parametric tests have been conducted on Battery BA-525 ( )/U, the 24 volt, 20 Ah size to establish its performance

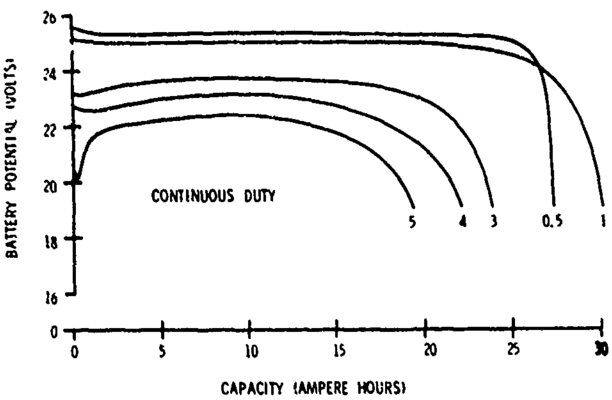


Figure 3. Effect of Constant Current Discharge on Battery Voltage and Capacity. The Curve Numbers Indicate the Discharge Rate in Amperes.

TABLE II

BA-525 ( )/U CHARACTERISTICS

LOAD	TEST TEMPERATURE 0° F (Cold)	0° F (Warm)	70° F	110° F	130° F
0.5 A	38.1 h 19.0 Ah		54.0 h 27.0 Ah		24.5 h 12.3 Ah
1 A	21.8 h 21.8 Ah	20.0 h 20.0 Ah	28.9 h 28.9 Ah		13.4 h 13.4 Ah
3 A	6.2 h 18.6 Ah	8.0 h 23.0 Ah	7.8 h 23.4 Ah	8.0 h 24.0 Ah	
4 A	5.3 h 21.2 Ah		5.3 h 21.2 Ah		3.5 h 14.0 Ah
5 A		4.4 h 22.0 Ah	3.8 h 19.0 Ah	0.3 h 1.5 Ah	

over a wide range of temperature and load conditions. These results are summarized in Table II and demonstrate the wide range over which these batteries will deliver their rated capacity. All capacities are for a battery voltage cutoff of 20 volts. Typical discharge curves for the discharges at 70°F shown in Table II are given in Fig. 3. These data can be related to the other batteries in the standard family by means of the data in Table III:

1. Room temperature operation. The zinc-air battery appears to provide its optimum performance at 70°F when reasonable currents are drawn. Results in the testing thus far on Battery BA-525 ( )/U which is rated at 20 Ah have ranged from 18.75 Ah at a 5 A drain which corresponds to a current density of 40 mA/cm² to 28.9 Ah for the 1 A drain. It should be noted that less than expected service is obtained at the 5 amp drain where more heat is generated and at the 0.5 amp drain where long service time provides for more water evaporation. Ordinarily continuous discharge conditions are more difficult for the zinc-air batteries in that more heat is produced. However, at room temperature, these differences are minimized. Room temperature intermittent discharges are shown in Fig. 4.[2]

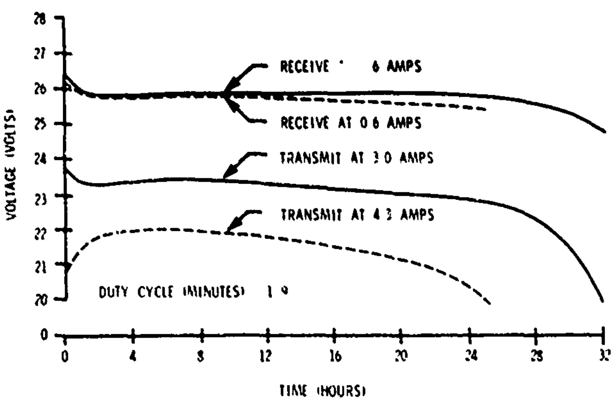


Figure 4. Transceiver Type Discharge at Ambient Room Temperature.

2. Low temperature operation--Thus far, low temperature testing at USAECOM on these batteries has not been extended below 0°F. Two types of starting conditions have been used as shown in Table II. In a cold start, the battery has been activated at room temperature then allowed to remain in an activated state at 0°F for at least 16 hours prior to applying a load. In a warm start, the unactivated battery and anodes were placed separately in the cold box at 0°F for at least 16 hours. The water at 40°F was placed in the cells and the battery activated with the cold anodes. After 15 minutes further at 0°F the load was applied to the battery in a 0°F ambient. With the warm battery start no difficulties were encountered. On loading the battery, starting voltages were all over 20 volts and discharge curves were much the same as room temperature curves except for a slight lowering of the peak voltage. In the cold start, however, some low starting voltages were encountered on the heavier drains. At 3 amperes the voltage dropped to 19 volts before recovery started and at 4 amperes the initial voltage dropped to 14 volts before starting to recover. This initial drop off in voltage is typical of zinc-air battery starts and is caused by oxygen depletion due to slow air velocity. When convective air flow is established, no further difficulties are found. Data in Table II are for continuous discharge. An example of transceiver type discharge is shown in Fig. 5.

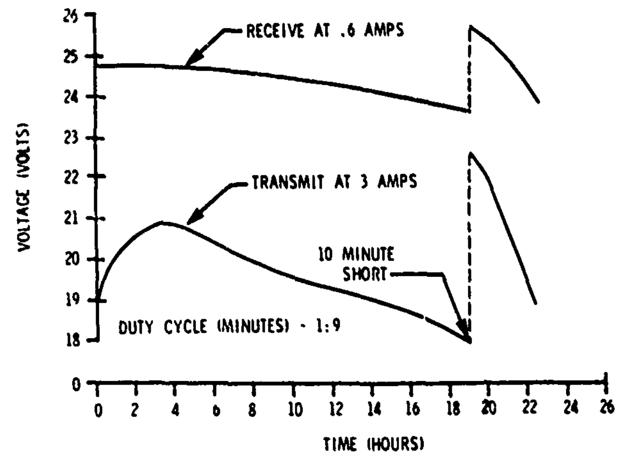


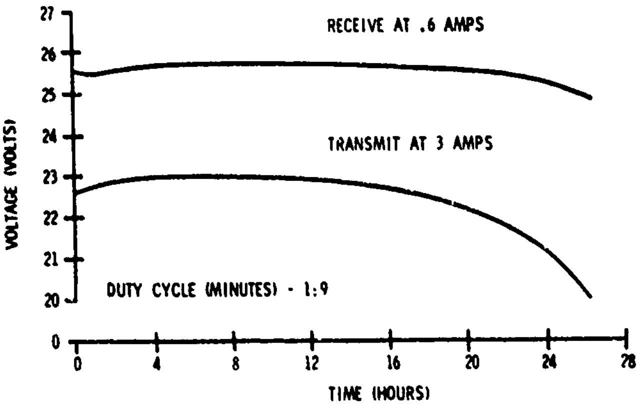
Figure 5. Transceiver Type Discharge at 0° F Ambient Temperature.

3. High temperature operation. The most strenuous conditions with which zinc-air batteries have to contend are those of high temperature. Here heat dissipation becomes a problem. Electrolyte vapor pressure rises and hot air flow will pick up

TABLE III

STANDARD LINE BATTERIES

CURRENT DENSITY mA/cm²	HRS. OF SERVICE	BATTERY TYPES BA-525 ( )/U	BA-526 ( )/U	BA-527 ( )/U	BA-530 ( )/U	BA-528 ( )/U
5	50	0.5 A	0.7 A	1.0 A	1.5 A	2.5 A
10	30	1.0 A	1.4 A	2.0 A	3.0 A	5.0 A
20	12.5	2.0 A	2.8 A	4.0 A	6.0 A	10.0 A
[illegible]	7	3.3 A	4.6 A	6.6 A	9.9 A	16.5 A
50	4	5.0 A	7.0 A	10.0 A	15.0 A	25.0 A



Fgiure 6. Transceiver Type Discharge at 125° F Ambient Temperature.

more moisture. In spite of this combination of difficulties, however, all batteries tested delivered over 60% of their rated capacity at 130°F on continuous discharge (See Table II). At 125°F, rated capacity was obtained on intermittent discharges on a simulated radio transmit and receive operation (see Fig. 6).

4. Cycle life. Another important consideration of zinc-air batteries is cycle life. At USAECOM we have been using Battery BA-539 ( )/U, consisting of 2 series connected 48 Ah standard line cells, for studying cycle life. Figure 7 shows the cycle life behavior of this 2-cell battery for 50 cycles, alternatively using anodes of two manufacturers. Considering that this battery is rated at 48 Ah, capacity to one volt per cell cutoff is still quite high. However, a 5% drop in the cell plateau voltage level was noted in both cases (Fig. 8).

5. Application Testing. In addition to the parametric testing for evaluation of the standard line battery capabilities, considerable effort at USAECOM has been devoted to our primary objective, that of providing power for military equipments. A considerable number and a wide variety of applications have been under investigation.

An important application is radio-transmitter equipment where the battery is required to operate on a light or receive load for the major period of its life, but be able to handle a heavy transit load on an intermittent basis. A typical duty cycle is a 1:9 ratio; 1 minute transmit, 9 minutes receive. An example of an intermittent discharge is the manpack Radio Set, AN/PRC-74. This is a 12 volt set and requires approximately 4.7 amps transmit and 0.110 amps receive current. Two standard line batteries a BA-525 ( )/U rated at 40 ampere hours capacity in the 12 V configuration and a BA-

Figure 7. Capacity vs Recharge Cycles in Endurance Tests on Zinc-Air Battery BA-539 ( )/U.

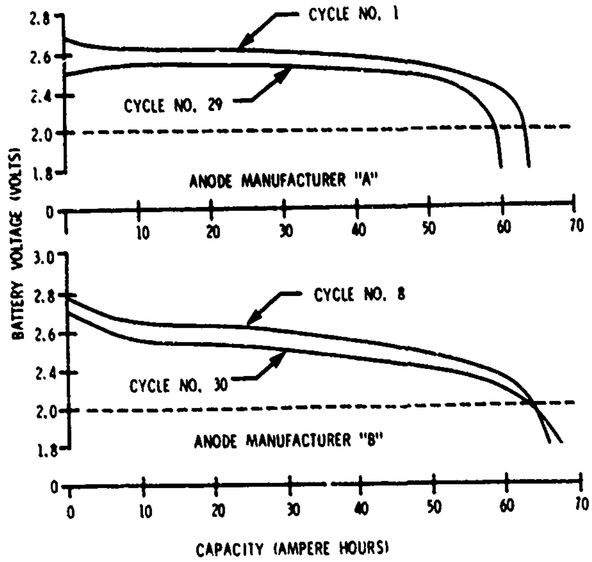


Figure 8. Effect of Cycle Life on Plateau Voltage Levels in Endurance Tests on Zinc-Air Battery BA-539 ( )/U.

527 ( )/U battery, 86 ampere hours, was used. The BA-525 ( )/U having the new type cathode with water reservoirs operated the set for 96 hours producing 54 ampere hours well above its rated capacity and consistent with the performance achieved on the continuous discharges shown in Table II. The BA-527 ( )/U having double the rated capacity, but proportionately smaller water reservoir operated the set for 128 hours for 75% of its rated capacity before moisture loss caused voltage depression below 10 volts

Surveillance equipment, such as radar sets and night vision equipments are good examples of continuous drain type of applications. Radar Set AN/PPS-5 requires a 6 volt, 60 watt battery. In order to fit the existing equipment, a zinc air battery was built into an existing battery box. Ten standard line cells of the 48 Ah size were used. The battery weighed 9 pounds and operated for over 11 hours at 60 watts continuous output, an energy output of over 70 watt-hours/pound, including the battery box.

The mechanically rechargeable zinc-air battery has demonstrated its compatibility on electrical and environmental tests to become an inportant power source for manpack and portable equipment. Its energy density, on practical, fully militarized batteries is in excess of 75 watt-hours per pound. The anode-replacement has been found to be a rapid, reliable, field-acceptable procedure for recharging. During the next year, more complete testing will be performed to characterize the batteries' capabilities under a wider variety of conditions. This will be supplemented by military potential, service and field testing to determine the performance under service and field conditions on a world-wide basis. With the satisfactory completion of the design and engineering, it is expected that the zinc-air battery will now commence its key role of powering critical forward area military equipments.

REFERENCES

1. D. Linden and H. R. Knapp, "Metal-Air Standard Family," Proc. 21st Annual Power Sources Conference, p. 109 (1967).
2. P. Noorily, "Development of Zinc/Air 24 Volt, 20 Ampere-Hour Standard Line Battery System," Final Report, Contract DAAB07-68-C-0265 (USAECOM), Leesona Moos Laboratories, Division of Leesona Corp., November 1968.